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(54) Method for manufacturing a dental prosthesis

(57) The invention relates to a method for manufacturing a fiber reinforced composite comprising the steps of (i) preparing a mould; (ii) filling the cavity of the mould with a fiber-reinforced polymerizable material comprising an organic matrix and a fiber component embedded within the matrix; (iii) applying pressure to the fiber-reinforced polymerizable material; and (iv) curing the fiber-reinforced polymerizable material. The method is characterized in that the mould is designed in a way which allows excess organic matrix material to escape form the cavity during pressing.

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Description

The invention relates to a method for manufacturing a fiber-reinforced composite especially a dental prosthesis such as a crown, bridge, implant superstructure, inlay bridge or removable dentures.

US-A-4,894,012 and WO 89/04640 disclose a two-step procedure for producing fiber-reinforced dental appliances. First, a fiber-reinforced composite material is produced having the requisite stiffness and strength characteristics and thereafter a dental device is formed therefrom. The composite material comprises essentially a polymeric matrix and a fiber component embedded within the matrix. The materials employed are preferably fully polymerized thermoplastic materials. Restorations such as e.g. bridges are prepared by heating the fiber-reinforced composite material with a heat gun until soft and then forming the material using a dental cast. Finally, acrylic teeth are fixed thereto.

US-A-5,098,304 discloses a method for reinforcing composite resin systems for restoring or splinting teeth which utilizes glass fiber material. Bridges are formed by first preparing the teeth which are adjacent to the missing tooth by grinding and then fixing a mesh or rope of fiber glass to the teeth. Thereafter a replacement tooth is formed on the fiber glass material.

US-A-5,176,951 and WO 91/11153 disclose a method of reinforcing a resin portion of a dental structure, which comprises the steps or applying one or more layers of a light weight woven fabric made up of polyaramide or polyethylene fibers to a resin portion of a dental structure and covering the woven fabric with more of the resin. In this method the fiber material and the resin have to be combined by the user when preparing the dental restoration. This is inconvenient and bears the risk of forming air pockets which cause destabilization of the restoration.

WO 95/08300 relates to a method for manufacturing a dental prostheses wherein a preimpregnated fabric part is placed on a shaping model and formed on the model by compression. Then the organic matrix of the preimpregnated fabric part is cross-linked to obtain a rigid support shell and successive layers of organic resin are applied onto the support shell to form an external finishing coating. The support shell comprises between 20 to 60 % by volume of fibers and other inorganic charges.

For producing fiber-reinforced bridges it is known to first prepare a dental cast which is partially covered with silicon to form a mould leaving a cavity for the restoration to be made. Then a preimpregnated fabric part is placed in the cavity, formed according to the model by compression and hardened. This process allows for the convenient preparation of metal free dental protheses. However, the use of preimpregnated fabric parts with a high fiber content requires high pressure during compressing. In contrast, use of preimpregnated fabric parts with a low fiber content result in restorations with a limited stability.

It is the object of the present invention to provide an improved method for manufacturing fiber reinforced composites with high fiber content from fabric parts or fiber material preimpregnated with an organic matrix which process does not require high pressure for forming the fiber reinforced material.

This problem is solved by a method for manufacturing an fiber reinforced composite comprising the steps of

(i) preparing a mould;
(ii) filling the cavity of the mould with a fiber-reinforced polymerizable material comprising an organic matrix and a fiber component embedded within the matrix;
(iii) applying pressure to the fiber reinforced polymerizable material; and
(iv) curing the fiber-reinforced polymerizable material.

This method is characterized in that the mould is designed in a way which allows excess organic material to escape from the cavity during pressing.

In a preferred embodiment the mould is provided with one or more grooves connecting the inside of the cavity with the outside of the mould. The grooves are cut into the mould from top to the bottom and allow matrix monomer to flow out of the mould after pressure has been applied. Thus, the volume fraction of fibers is increased remarkably and the strength of the composite is increased.

A schematic view of a mould provided with a plurality of grooves is shown in Figure 1. The grooves are preferably 0.05 to 1.5 mm wide, more preferably 0.05 to 1.0 mm, most preferably 0.2 to 1.0 mm.

Another way to increase the volume fraction of fibers is to form one or more drainages. A schematic view of a mould provided with two drainages is shown in Figure 2. The drainages preferably have a inner diameter of from 0.05 to 1.5 mm, more preferably 0.05 to 1.0 mm, most preferably 0.2 to 1.0 mm.

The grooves and/or drainages should be applied on both sides of the cavity. The number of grooves and drainages depends on the size of the cavity. Moulds for the preparation of a dental bridge are usually provided with 2 to 4 grooves and/or drainages on each side of the mould, preferably 1 groove or drainage every 5 mm, more preferably 1 groove or drainage every 3 mm.

Still a further way to increase the volume fraction of fibers is to provide the mould with void space able to take up excess matrix material. A preferred way of providing void space is to make a bevelled cavity as is schematically shown

a great resistance to abrasion and a colour shade close to that of the natural tooth. Charged cosmetic resins of this kind are known as such.

Table 1

Compositions of most preferred fiber-reinforced polymerizable materials			
Composition	**Composition No.1** (% by weight)	**Composition No. 2** (% by weight)	**Composition No. 3** (% by weight)
Bis-GMA	38.6	24.5	35.2
Decandiol dimethacrylate	0.5	03	0.4
Triethyleneglycol dimethacrylate	9.7	6.2	8.8
Urethane dimethacrylate	0.1	0.1	0.1
High dispersed silica	5.5	3.5	5.0
Catalysts and Stabilizers	<0.5	< 03	< 0.4
Pigments	<0.1	<0.1	<0.1
Glass fibers	45.0	65.0	50.0

It has been found that the fiber content of a fiber-reinforced composite could be increased for instance from 43.3 vol.% to 47.7 vol.% if the material is compressed in a mould according to the present invention using a pressure of about 2 bar (Table 2). This is an increase of the fiber content more than 10 %. The increase of fiber content resulted in an increase of flexible strength and modulus of elasticity of about 15 %.

The fiber content of the fiber-reinforced composites comprising inorganic fibers is determined via loss of ignition (LOI). The organic matrix material of the fiber-reinforced composite is burned at 850 °C for 1.5 hours and the inorganic reminder (ash or loss of ignition, LOI) determined gravimetrically. The relation between LOI and the volume fraction of fibers for Compositions No. 1, No. 2 and No. 3 is shown in Figure 5. As can be seen LOI and volume fraction of fibers are linearly correlated. By linar regression analysis the following equation can be derived from Figure 5:

$$\text{vol.\%} = 1.064 \times \text{LOI} - 23.4$$

The fiber content of fiber-reinforced composites comprising organic fibers can be determined by scanning electron mircroscopy.

It was further found that the modulus of elasticity and the flexural strength are linearly correlated to the volume fraction of fibers in percent. Thus, fiber-reinforced composites having the desired physical properties can be produced by adjusting the volume fraction of fibers to a suitable value. Figures 6 and 7 show the relationship between flexural strength and modulus of elasticity, respectively, and the volume fraction of fibers for the preferred material No. 1, and Figures 8 and 9 for the preferred material No. 2.

The fiber-reinforced composite obtained after the first curing step may be further improved by implying additional layers of fiber-reinforced polymerizable material. For this purpose the mould is preferably cut back to lay bare the dental cast and to form a die. Further layers of fiber-reinforced polymerizable material are placed on the die as shown schematically in Figure 10. Figure 10 shows a die placed in a machine as shown in Figure 4. During pressure application the membrane presses the fiber-reinforced polymerizable material on the die. Hardening is achieved by photopolymerisation.

It was found that the fiber content of the additional layers is influenced by the form of the die. To increase the strength of the fiber-reinforced composite it is preferable to make a narrow shoulder as is schematicly shown in Figure 11, i.e. the shoulder follows the line of the wall of the tooth to be restored and steps are to be avoided. The term "narrow shoulder" refers to shoulders with steps preferably having an edge length of 0 to 1.0 mm, more preferably 0 to 0.5 mm.

For manufacturing e.g. a crown it is usually not necessary to prepare a mould. In this case the fiber-reinforced composite is prepared by

(1) first preparing a cast of the tooth which is to be restored;

(2) applying a covering agent to the model and the cast to cover the cast and leaving only the tooth to be restored uncovered;

(3) placing a fiber-reinforced polymerizable material comprising an organic matrix and a fiber component embedded onto the uncovered tooth;
(4) applying pressure to the fiber-reinforced polymerizable material;
(5) curing the fiber-reinforced polymerizable material.

The shoulder of the die is preferably formed as discussed above.

Figure 12 shows a picture of a electron microphotograph of fiber-reinforced composite prepared by use of a narrow shoulder and Figure 13 of a fiber-reinforced composite prepared by use of a wide shoulder. The volume fraction of fibers was measured at three different sections of the fiber-reinforced composite by determining the LOI of different sections of the composite. In the composite produced by use of a narrow shoulder the fiber content ranges from 30 to 41 % whereas in case of the wide shoulder a fiber content from 23 to 41 % was found. The strength of the fiber-reinforced composites can be determined by use of the graphs of Figures 6 to 9.

In the following the present invention will be further illustrated by use examples.

Example 1

A silicon mould with a cavity of 3 x 3 x 36 mm was made. The cavity was filed with material No. 2 (see Table 1 above) and covered with an elastic membrane. The membrane was pressed onto the mould with a pressure of approximately 2 bar in a machine as shown in Figure 4 (VECTRIS® VS1, Ivoclar). 2 minutes after pressure application the light source was switched on and the material cured within 7 minutes. In a first test series the cavity of the mould was underfilled, in a second series overfilled. This procedure was repeated with moulds provided with a 3 grooves having a width of 1 mm or 2 drainages having a inner diameter of 1 mm on each side. In a further test bevelled and non-bevelled moulds were used. The flexural strength and the modulus of elasticity of the bodies prepared was tested according to ISO 10477. The results are shown in Table 2.

Table 2 shows that moulds with grooves and drainage tubes generally result in a higher fiber content. The highest strength and fiber volume was achieved with an overfilled mould with grooves. Bevelled moulds also resulted in an increase of fiber content and strength.

Table 2

Fiber content and mechanical properties of fiber reinforced composites				
		mould without drainage	**mould with grooves**	**mould with drainage tubes**
underfilled not bevelled	ash	61.2 %	61.8 %	61.5 %
	Vol.fraction in %	41.7 %v	42.3 %v	42.2 %v
	flexural strength	1105 MPa	1129 MPa	1125 MPa
	modulus of elast.	37140 MPa	37936 MPa	37804 MPa
overfilled not bevelled	ash	62.7 %	66.8 %	65.1 %
	Vol.fraction in %	43.3 %v	47.7 %v	45.9 %v
	flexural strength	1170 MPa	1347 MPa	1275 MPa
	modulus of elast.	39263 MPa	45101 MPa	42713 MPa
underfilled bevelled	ash	61.6 %	63.5 %	63.8 %
	Vol.fraction in %	42.1 %v	44.1 %v	44.5 %v
	flexural strength	1121 MPa	1202 MPa	1218 MPa
	modulus of elast.	37671 MPa	40325 MPa	40855 MPa
overfilled bevelled	ash	60.6 %	64.9 %	62.8 %
	Vol.fraction in %	40.8 %v	45.4 %v	43.2 %v
	flexural strength	1068 MPa	1254 MPa	1165 MPa
	modulus of elast.	35946 MPa	42048 MPa	39130 MPa

Example 2

A dental cast was made from a tooth prepared for receiving a crown. The cast was covered with condensation silicon mass (Optosil®, Bayer) in a way that only the tooth stump to be restored remained uncovered. In the first test a narrow silicon shoulder was prepared and in the second test a wide shoulder. A disc shaped preimpregnated fabric part (Table 1, No. 1) was placed on the stump and shaped on the model by compression with a flexible membrane as shown in Figure 10. The preimpregnated fabric part was light cured as described in Example 1. Then the fiber content at three different sections of the fiber-reinforced composite was determined by cutting the composite into pieces and measuring the LOI (% ash). The strength at the three sections was estimated using the graphs of Figures 7 and 8. The results are shown in Table 3 and Figures 12 and 13.

Table 3

Fiber content and mechanical properties in different sections of fiber reinforced coposites			
		Narrow silicone shoulder	**wide silicone shoulder**
occlusal section	% ash (LOI)	60.9 %	60.6 %
	Vol.fraction in %	41.4 %v	41.1 %v
	flexural strength	892 MPa	883 MPa
	modulus of elasticity	29094 MPa	28762 MPa
middle section	ash	565 %	44 %
	Vol.fraction in %	36.7 %v	23.4 %v
	flexural strength	757 MPa	376 MPa
	modulus of elasticity	23887 MPa	9153 MPa
gingival section	ash	50.5 %	43.5 %
	Vol.fraction in %	30.3 %v	22.9 %v
	flexural strength	574 MPa	361 MPa
	modulus of elasticity	16797 MPa	8599 MPa

Claims

1. A method for manufacturing a fiber reinforced composite comprising the steps of

   (i) preparing a mould;
   (ii) filling the cavity of the mould with a fiber-reinforced polymerizable material comprising an organic matrix and a fiber component embedded within the matrix;
   (iii) applying pressure to the fiber-reinforced polymerizable material; and
   (iv) curing the fiber-reinforced polymerizable material **characterized in that** the mould is designed in a way which allows excess organic matrix material to escape form the cavity during pressing.

2. A method according to claim 1, **characterized in that** the mould is provided with one or more grooves connecting the inside of the cavity with the outside of the mould.

3. A method according to claim 2, **characterized in that** the grooves are 0.05 to 1.0 mm wide.

4. A method according to anyone of claims 1 to 3, **characterized in that** the mould is provided with one or more drainages.

5. A method according to anyone of claims 1 to 4, **characterized in that** the cavity is provided with a void space able to take up excess matrix material.

6. A method according to claim 5, **characterized in that** the cavity is bevelled.

7. A method according to anyone of claims 1 to 6, **characterized in that** the fiber-reinforced polymerizable material comprises glass, ceramic and/or silica fibers.

8. A method according to anyone of claims 1 to 7, **characterized in that** the fiber-reinforced polymerizable material comprises 45.0 to 65.0 % by weight of the fiber component.

9. A method according to anyone of claims 1 to 8, **characterized in that** the fiber-reinforced polymerizable material comprises 31.1 to 48.9 % by weight of the organic matrix material.

10. A method according ot anyone of claims 1 to 9, **characterized in that** the fiber-reinforced polymerizable material comprises a methacrylate resin, dimethacrylate resin, dimethacrylate-based aromatic resin, epoxy-based aromatic resin, polymethacrylate resin and/or urethane methacrylate resin.

11. A method according to anyone of claims 1 to 10, **characterized in that** the fiber-reinforced polymerizable material comprises a mixture of Bis-GMA, decandiol dimethacrylate, triethyleneglycol dimethacrylate and urethane dimethacrylate.

12. A method according to claim 11, **characterized in that** the mixture comprises 24.5 to 38.6 % by weight Bis-GMA, 0.3 to 0.5 % by weight decandiol dimethacrylate, 6.2 to 9.7 % by weight triethyleneglycol dimethacrylate and 0.1 % by weight urethane dimethacrylate.

13. A method according to claim 12, **characterized in that** a fiber-reinforced polymerizable material comprising 24.5 % by weight Bis-GMA, 0.3 % by weight decandiol dimethacrylate, 6.2 % by weight triethyleneglycol dimethacrylate, 0.1 % by weight urethan dimethacrylate, 3.5 % by weight high dispersed silica, < 0.3 % by weight catalysts and stabilizers, < 0.1 % by weight pigments and 65.0 % by weight glass fibers is used.

14. A method according to anyone of claims 1 to 13, **characterized in that** an elastic membrane is used for applying pressure.

15. A method according to anyone of claims 1 to 14, **characterized in that** a pressure of about 2 bar is applied.

16. A method according to anyone of claims 1 to 15, **characterized in that** the polymerizable fiber-reinforced material is hardened by light curing.

17. A method according to claims 1 to 16, **characterized in that** the cavity of the mould is overfilled.

18. A method according to anyone of claims 1 to 17, **characterized in that** the mould is a silicone mould.

19. A method according to anyone of claims 1 to 18, **characterized in that** the fiber reinforced composite is a dental restoration.

20. A method for manufacturing a fiber reinforced composite comprising the steps of

(1) preparing a cast of the tooth which is to be restored;
(2) applying a covering agent to the model and the cast to cover the cast and leaving only the tooth to be restored uncovered;
(3) placing a fiber-reinforced polymerizable material comprising an organic matrix and a fiber component embedded onto the uncovered tooth;
(4) applying pressure to the fiber-reinforced polymerizable material;
(5) curing the fiber-reinforced polymerizable material **characterized in that** the covering agent is applied in a way such that a narrow shoulder is formed, i.e. the shoulder follows the line of the wall of the tooth to be restored.

21. Method according to claim 20, **characterized in that** a silicon covering agent is used.

Figure 1

Schematic view of a mould provided with grooves

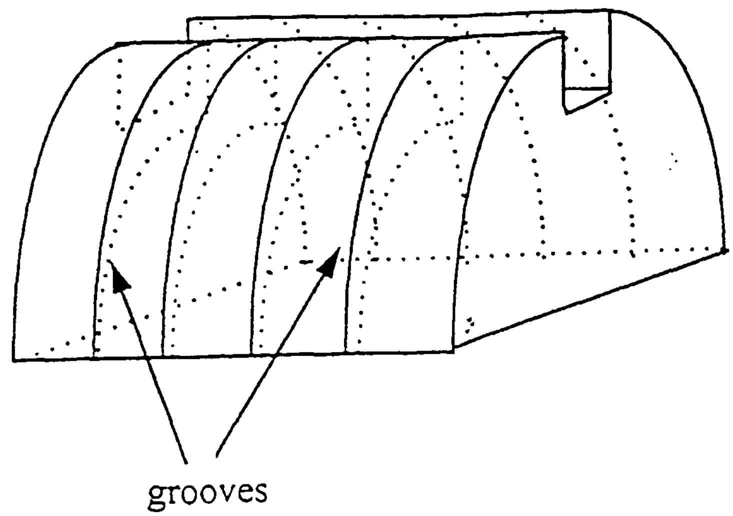


Figure 2

Schematic view of a mould provided with drainages

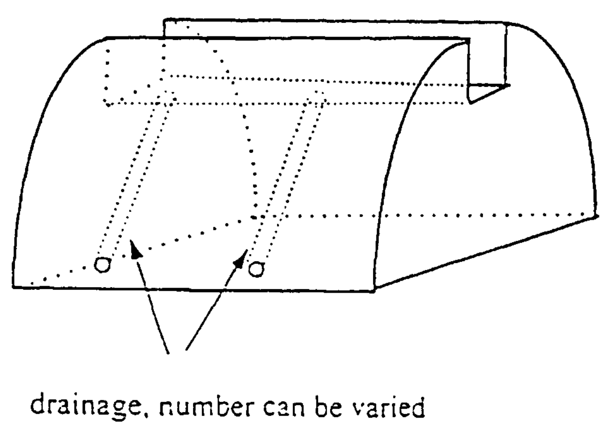


Figure 3

Schematic view of a mould with a bevelled cavity

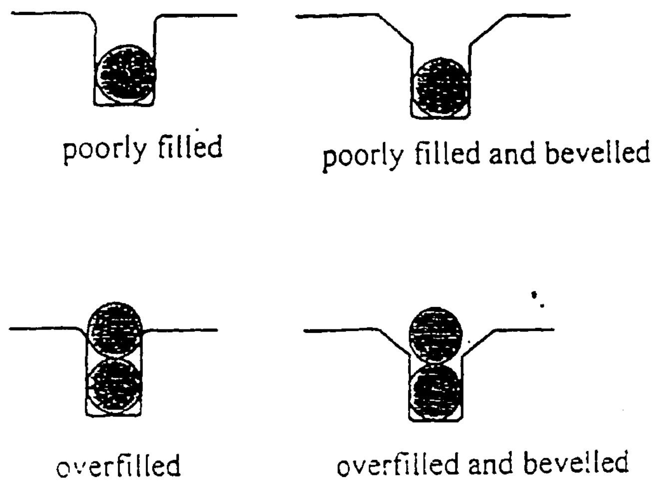


Figure 4

Schematic vertical sectional view of a machine
for forming fiber-reinforced composites

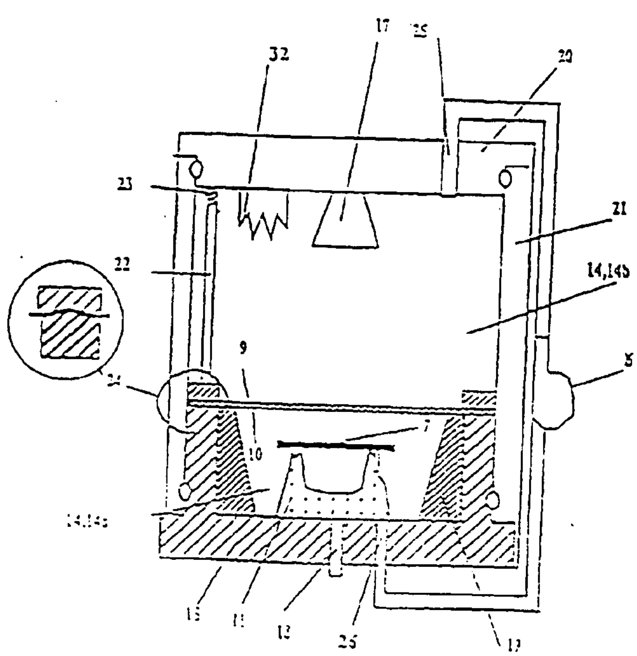
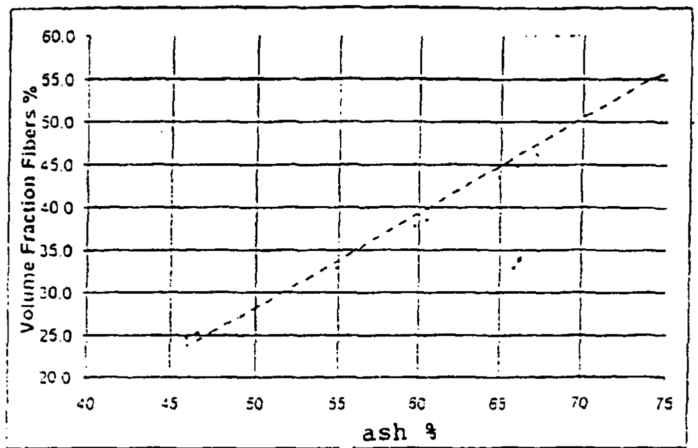


Figure 5

Relation between volume fraction of fibers
and Loss of ignition (LOI)



graph 1: The volume fraction of Fibers can be calculated using the loss of ignition.

Figure 6

Relation between volume fraction of fibers and
flexural strength (composition No. 1)

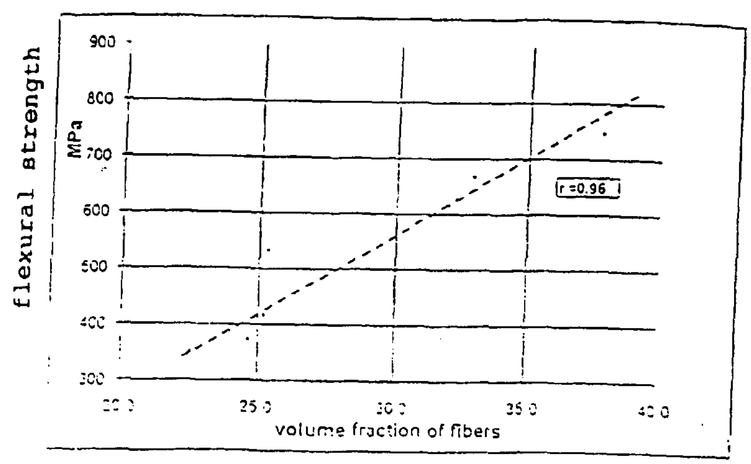


Figure 7

Relation between volume fraction of fibers and modulus of elasticity (composition No. 1)

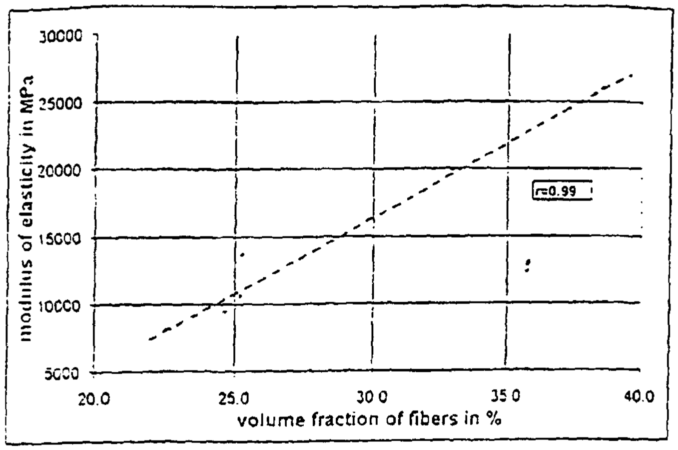


Figure 8

Relation between volume fraction of fibers and flexural strength (composition No. 2)

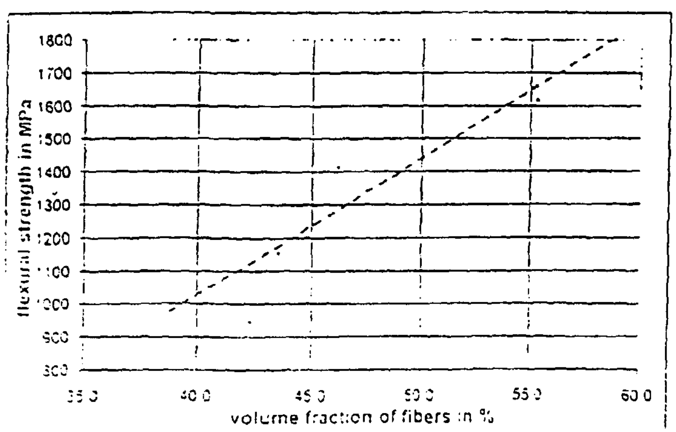


Figure 9

Relation between volume fraction of fibers and modulus of elasticity (composition No. 2)

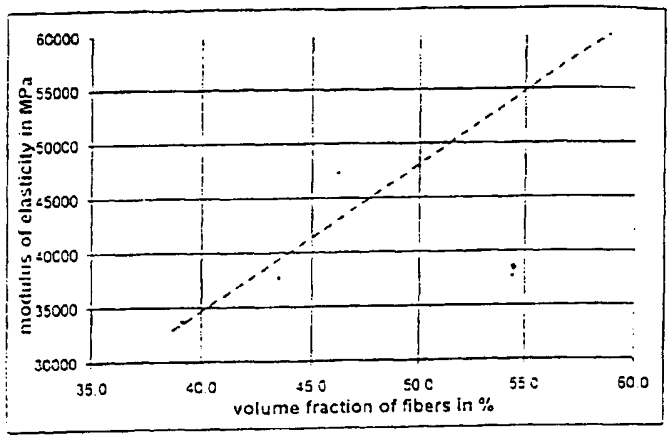


Figure 10

Schematic view of the operating principle of the machine according to Fig. 4

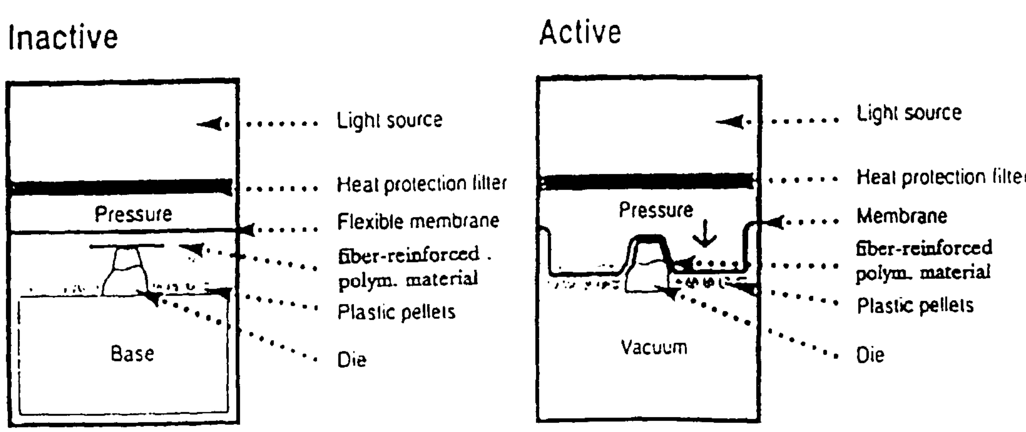


Figure 11

Schematic view of a die with a narrow/wide shoulder

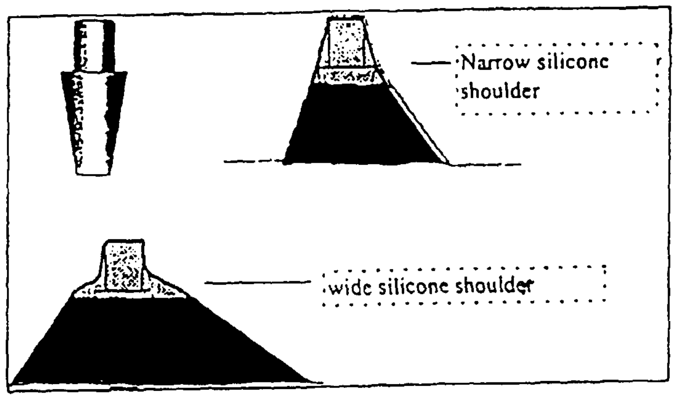


Figure 12

Electron microphotograph of a crown prepared with a die having narrow shoulder

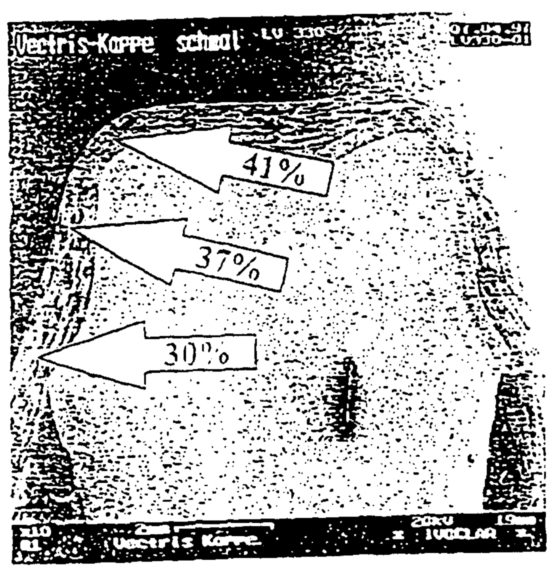


Figure 13

Electron microphotograph of a crown prepared with a die having a wide shoulder